

# INVESTIGATION OF THE MAKING OF HIGH-MODULUS SODIUM SILICATE FROM SULFATE BATCH WITHOUT USING A REDUCER

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The results of computational and experimental investigations of making trimodular sodium silicate from sulfate batch without using a reducer are presented. The results presented attest that there are great possibilities of organizing a process for making sodium silicate without using a reducer at temperatures 1450–1500°C in thin films of melt.

**Key words:** soluble glass, sodium silicate, sodium sulfate, sulfate batch, sulfate wastes, reducer, reduction, glassmaking, decomposition, evaporation.

Soluble sodium silicate is produced by the dry method using as the alkaline component soda or a mixture of soda and sodium sulfate as a minor additive in the amounts 1–5% (mass fraction) of the total content of alkaline components in the batch [1]. The complete replacement of soda by sodium sulfate or sulfate wastes, which are formed in large quantities in a number of sectors of the chemical industry [2], is of special interest owing to economic and environmental advantages.

Historically the existing sulfate methods of making soluble glass are based on the interaction of sodium sulfate  $\text{Na}_2\text{SO}_4$  with silica in the presence of a reducer: carbon (5–7%) or solid substances containing carbon (coke, charcoal, coal-tar pitch, and others) [3]. In its presence the interaction of  $\text{Na}_2\text{SO}_4$  and  $\text{SiO}_2$  is significantly accelerated, as a result of which the glassmaking temperature is lower 1250–1300°C. However, this method has a number of drawbacks that complicate the technological process significantly [3]:

- deficiency or excess of reducer causes liquation of the melt, which manifests in the formation of a foamy surface layer, called halmoz;
- sodium sulfide forms in the presence of elevated content of reducer in the mixture and reacts with iron oxides which results in the formation  $\text{FeS}$ , which colors the soluble glass;
- the glassmaking process gives rise to active corrosion of furnace refractories and, in general, gives lower-quality products;

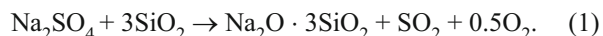
– the process is accompanied by the formation of the sulfur oxide  $\text{COS}$ , which is a very poisonous gas.

There are a number of patents (RU 2379233, RU 2345951, RU 2151100 and others) describing different methods of producing sodium silicate from sulfate wastes produced in different chemical production operations characterized by a number of particularities:

- sulfate wastes containing substances with reducing components ( $\text{C}$ ,  $\text{C}_n\text{H}_m$  and so on) will make it possible to go without the adding additional reducer to the batch; the volume of such wastes does not exceed 10–15% of all existing sulfate wastes, suitable in the production of silicate blocks;
- use of highly energy-intensive technologies which are not competitive under the current market conditions.

The current conditions make it necessary to develop an efficient resource- and energy-conserving technology for producing high-modulus sodium silicate, widely used in many sectors of the national economy.

To determine the possibility of obtaining high-modulus sodium silicate ( $m = 3$ ) from sulfate batch without using a reducer a thermodynamic analysis was performed by the method of M. I. Temkin and L. A. Shvartsman in the temperature interval from 1000 to 2000 K according to the reaction



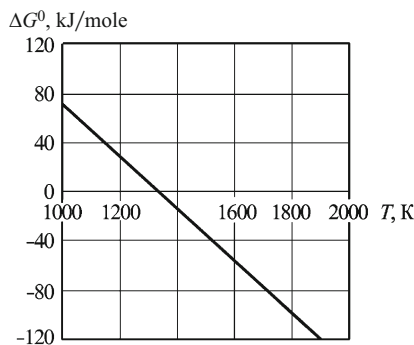
The basic working equation for determining the isobaric-isothermal potential  $\Delta G^0$  (Gibbs energy) determining the fundamental possibility of the chemical reaction by the indicated method is

$$\Delta G^0 = \Delta H_{298}^0 - T \Delta S_{298}^0 - T \int_{298}^T \frac{dT}{T^2} \int_{298}^T \Delta c_p dT, \quad (2)$$

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**Fig. 1.** Change in the Gibbs energy in the temperature interval from 1000 to 2000 K.

where  $\Delta H_{298}^0$  and  $\Delta S_{298}^0$  are, respectively, the standard heat and entropy change in the chemical reaction.

The temperature dependence of the specific heat is given by the equation

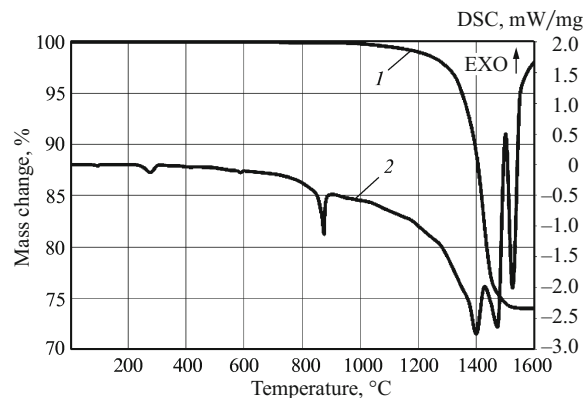
$$\Delta c_p = \Delta a + \Delta b T + \Delta c' T^{-2}, \quad (3)$$

where  $\Delta a$ ,  $\Delta b$  and  $\Delta c$  are the algebraic sums of the constant coefficients of like powers of  $T$  in the equations for the specific heat of the reagents taking account of the stoichiometric coefficients in the reaction equation.

The results of the calculation of the change in Gibbs energy  $\Delta G^0$  for the reaction (1) are presented in Fig. 1.

As one can see from Fig. 1, the Gibbs energy  $\Delta G^0$  of the reaction (1) is negative at temperatures above 1366 K, which indicates a possibility of obtaining sodium silicate from a sulfate batch without the need for using a reducer. It should be noted that as the temperature increases, the negative values of  $\Delta G^0$  attest to a high probability of the reaction going to completion.

To confirm the possibility of the reaction (1) occurring, thermogravimetric studies of the process of making sodium silicate with silicate modulus 3.2 from weighed quantities of sulfate batch in the temperature interval 20 – 1600°C in a platinum-rhodium crucible in atmospheric air were performed in an STA 449 F1 Jupiter synchronous thermal analyzer from the Netzsch company with the gases released being determined with a TENSOR Fourier IR-Spectrometer from the Bruker Optik Company.



**Fig. 2.** Thermogravimetry of a weighed portion of sulfate batch in the temperature interval 20 – 1600°C (heating rate 10 K/min).

The composition of the sulfate batch and the chemical composition of the initial raw materials are presented in Table 1.

It was determined in the course of the experiments that an active interaction reaction between the silica and sodium sulfate starts at temperatures 1300 – 1350°C (Fig. 2). This is confirmed by a sharp reduction of the mass of the weighed amount of sulfate batch with  $\text{SO}_2$  being released (Fig. 3). The cooking of the molten glass is completed in the temperature interval 1400 – 1500°C.

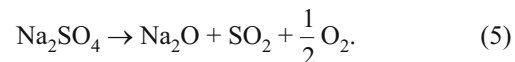
It is worth noting that sodium sulfate boils are about 1400°C [4]. Significant evaporation can make it impossible to obtain sodium silicate by means of the reaction (1).

For complete evaporation of sodium sulfate from the sulfate batch with the adopted composition (see Table 1) according to the reaction (4) the mass of the weighed portion should have decreased by 42%:



However, in the experiment the total loss of mass was 26% (see Fig. 2), which is 1.6 time smaller.

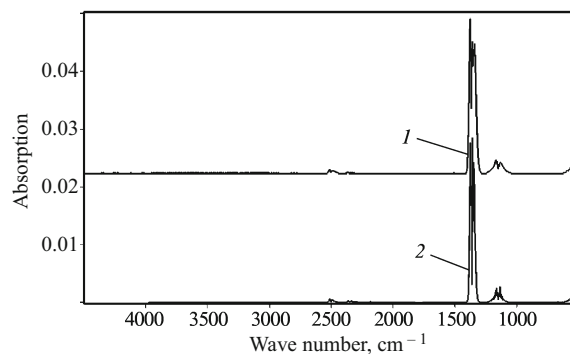
For thermal decomposition of sodium sulfate near the boiling point according to the reaction (5) the maximum mass loss should be 18.3%:



The real mass loss in the experiment is somewhat larger. This can be explained by the evaporation (4) and decomposi-

**TABLE 1.** Composition of the Sulfate Batch and Chemical Composition of the Initial Raw Materials

Raw material	Oxide content, wt.%						Content in batch, %
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO} + \text{MgO}$	$\text{Na}_2\text{SO}_4$	Other	
Sodium sulfate, chemically pure grade, GOST 4166–76	–	–	–	–	99.5	0.50	58
Quartz sand, VS-040-1 grade, GOST 22551–77	98.5	0.6	0.04	–	–	0.86	42



**Fig. 3.** IR spectrum of released gases at 1340°C, CO<sub>2</sub> and H<sub>2</sub>O signals removed (1), compared with the SO<sub>2</sub> spectrum (2) presented in the literature.

tion (5) processes occurring in parallel. The fraction  $k$  of the decomposed sodium sulfate can be calculated from the equation

$$k \times 18.3 + (1 - k) \times 100 = 26.0, \quad (6)$$

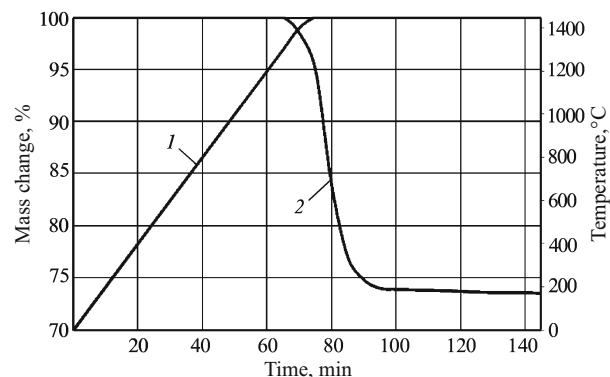
from which  $k = 0.906$ , or 90.6%. Correspondingly, the evaporated sodium sulfate fraction in the experiment equals  $(1 - k) = 0.094$ , or 9.4%, including calcination losses of the weighed portion of the sulfate batch.

To check for the presence of significant evaporation of sodium sulfate an additional experiment was performed on making sodium silicate from sulfate batch with isothermal soaking at 1450°C for 1 h in atmospheric air (Fig. 4).

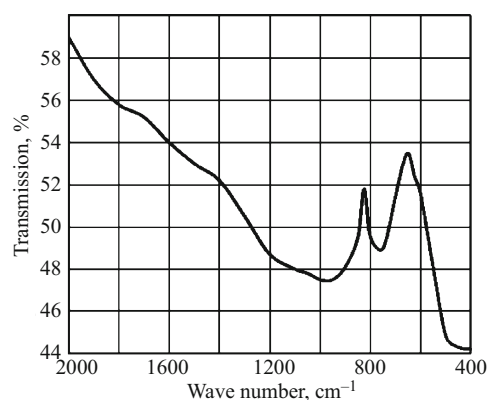
As one can see from Fig. 4, the glassmaking process is completed in 20–25 min, and the mass loss of the weighed portion does not exceed 27%. Thus, the discrepancy between the experimental results and the maximum theoretical mass losses according to the reaction Eq. (5) according to the prescribed silicate modulus in both cases is no more than 9%, which gives grounds for the possibility of organizing the production of high-modulus sodium silicate in the temperature interval 1450–1500°C with negligible losses of sodium sulfate.

The results of the investigation of experiments with weighed portions of sulfate batch (0.03–0.06 kg) in a Nabertherm HT08/17 electric furnace in a platinum-rhodium crucible in atmospheric air confirmed that at 1450–1500°C at least 20–25 min are required to make the glass. However, an increase of the surface density of the weighed portion of sulfate batch to greater than 500 kg/m<sup>2</sup> makes it possible to produce sodium silicate with silicate modulus 3.2. This is because the unreacted sodium sulfate rising to the surface of the melt evaporates, which is indicated by the large mass loss of the weight portion of sulfate batch.

Analysis of the infrared spectrum of the sodium silicate, presented in Fig. 5, in the experimental region 2000–400 cm<sup>−1</sup> showed that the spectrum obtained corresponds to the compound Na<sub>2</sub>O · 3SiO<sub>2</sub>. This sodium silicate consists of a number of wide diffuse bands due to the fundamental vi-



**Fig. 4.** Making sodium silicate from sulfate batch with isothermal soaking: 1) temperature; 2) mass change.



**Fig. 5.** IR spectrum of sodium silicate glass made from sulfate batch.

brations of silicon and oxygen atoms in the silicon-oxygen base of the glass, and the absence of bands characteristic for sulfur-containing functional groups entering into the composition of the compounds.

The present investigations of the production of high-modulus sodium silicate from sulfate batch attest to the great possibilities of organizing a process for making sodium silicate without using reducers at temperatures 1450–1500°C in the films of melt.

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